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EP1.89/2:B63/6

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development | EPA-600/S2-81-081 Mar. 1982

EPA

Project Summary

ORIGINAL

REVISED
This Project Summary rescinds and replaces one previously issued bearing the same number, a similar title, and dated August 1981.

Characterization of Boliden's Sulfide-Lime Precipitation Plant

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Sulfide precipitation is an effective process for the treatment of industrial wastes containing highly toxic heavy metals. The attractive features of the sulfide precipitation process are: attainment of high degree of metal removals over a broad pH range, effective precipitation of certain metals (such as: As, Cu, Cd, Hg) even at very low pH, low detention time requirement in the reaction tank because of the high reactivity of sulfides, and the feasibility of selective metal recovery. With sulfide precipitation, the high reactivity of sulfides (S^{2-}, HS^-, H_2S) with heavy metal ions and the very low solubilities of the heavy metal sulfides over a broad pH range are features not found with the hydroxide precipitation processes.

Sulfide precipitation processes to remove heavy metals have gained considerable importance.[1-6] Bhattacharyya, et al.[3,4] have done extensive bench-scale sulfide precipitation work at the University of Kentucky. High degree of separation of heavy metal cations and arsenic from actual smelter effluents was obtained with a combination lime-sulfide precipitation process. During the second phase of the project a joint work (by University of Kentucky, Radian Corporation, and Boliden Metall Corporation, Sweden) was undertaken to obtain *full-scale* sulfide precipitation data from a unique system (to remove arsenic, heavy metals and fluoride) recently developed by a Swedish nonferrous metal production (copper and lead smelter) company. The full-scale plant (200 m^3/hour capacity) was put into operation in 1978 and was designed to precipitate (at pH 3-5) As, Zn, Cu, Pb, Cd, and Hg as sulfide for possible recycle to "roaster," and remove fluoride separately by lime (at pH > 10) as CaF_2 (uncontaminated with heavy metals) for landfill. The of an investigation involving both *full-scale* results and laboratory-scale precipitation of metals (from nonferrous metal production operations) are presented.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Experimental

The full-scale data was obtained at Boliden Metall Corporation, Skellefte-hamn, Sweden. The system was designed to treat process water, and rain and wash waters as a single waste stream to maximize containment of heavy metals at a reasonable cost. The process water was typically 30 to 40% of the total flow.

Plant Description. A schematic diagram of the process is shown in Figure 1. The wastewaters contained heavy metals and were normally acidic. The major constituents were arsenic (100-500 mg/l) and zinc (25-200 mg/l). Cop-

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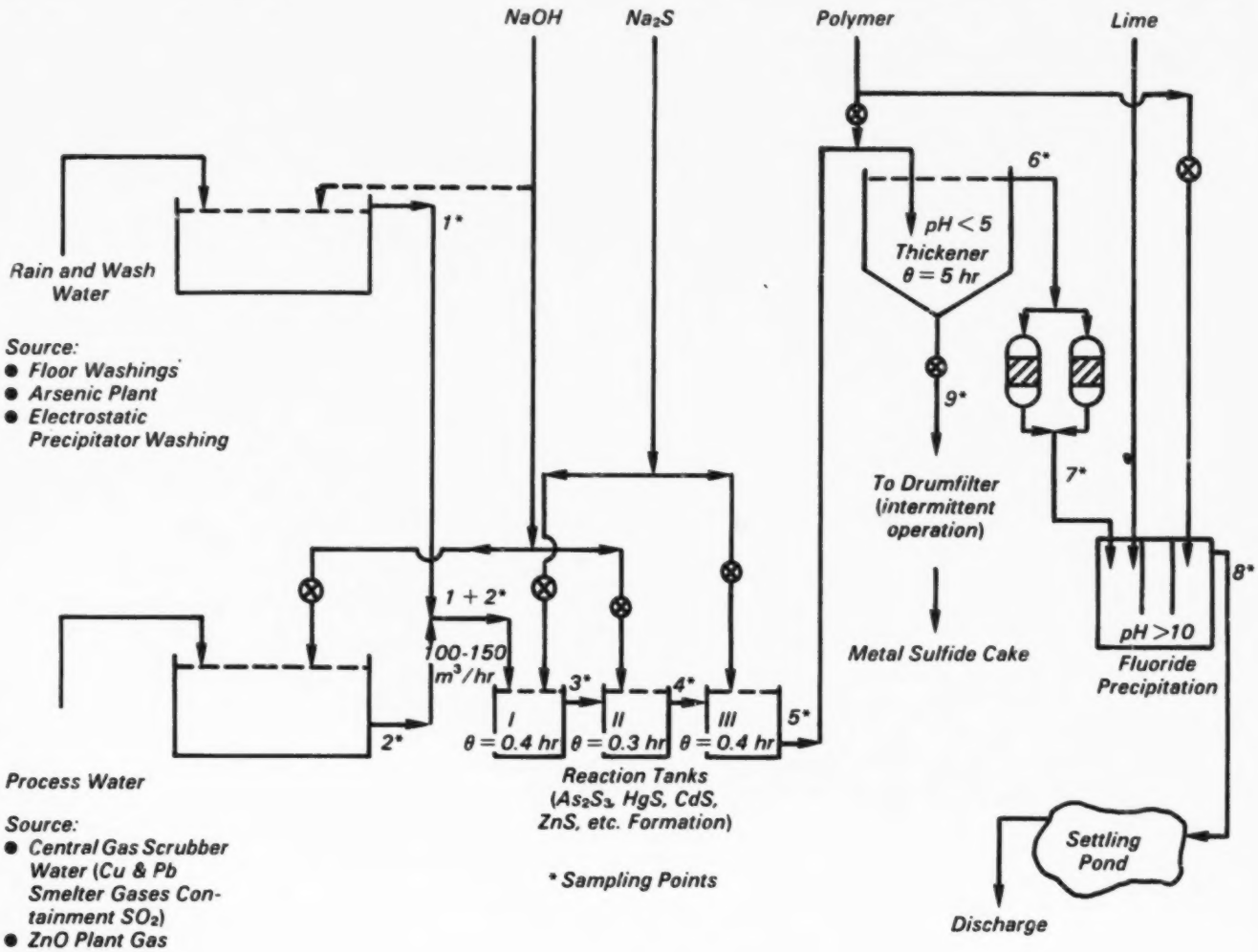

Figure 1. *Schematic diagram of the full-scale sulfide-lime treatment process.*

per, lead, mercury, and selenium were present in smaller amounts (a total of 40 mg/l). The incoming water was first partly neutralized (with NaOH) to pH 2.5-3.0, then sodium sulfide was added. The amount of reagent added was controlled by monitoring the pH, i.e., the addition of sodium sulfide was stopped when a predetermined pH value was reached.

Sodium sulfide was added as a 15 percent solution to the first reaction tank, which had a 55 m^3 capacity. This resulted in a wastewater residence time of between 20 and 30 minutes at flow rates of 110 to 170 m^3/h. The third reaction tank was also equipped to allow the addition of more sulfide. This was sometimes necessary in order to compensate for secondary reactions. The wastewater-precipitate slurry was pumped from the third reaction tank to a thickener where flocculant was added to enhance sedimentation properties. The sludge from the thickener underflow was further concentrated by using a belt drum filter. The filtrate was returned to the reaction tanks. The overflow from the thickener was polished in one of two parallel multilayer filters. The effluent from the polishing step was fed to the fluoride treatment plant. A 10 percent lime slurry was added to adjust the pH to 10 or greater. The CaF_2 slurry was pumped to a settling pond. The overflow from this settling pond was fed to an intermediate holding pond for discharge to the smelter effluent receiver.

The 15 percent Na_2S solution and the 10 percent lime slurry were prepared within the plant. The 40 percent sodium hydroxide solution was purchased commercially. The mixing tanks were instrumented with level controls. Occasional

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overflows from these mix tanks were directed to the exit stream of the CaF_2 precipitation tank.

Although, the full-scale plant had been in operation for approximately one year, the plant was still considered to be in a startup mode, due to the operational problems related to a higher than anticipated arsenic level in the waters treated.

Process Evaluation. The full-scale process was evaluated in 1979. A test plan was devised to determine the heavy metal and arsenic removal of the overall process in three short tests (ST-01, ST-02, ST-03), and to determine the performance of the individual process vessels in two more detailed or "long" tests (LT-01 and LT-02). The important sampling points are shown in Figure 1. For the short tests only the incoming streams (Points 1 and 2) and the effluent stream (Points 7 and 8) were sampled.

Laboratory Studies. Bench-scale studies were also conducted at the University of Kentucky to identify the effects of pH and sulfide dosage on arsenic and zinc separations. In the full-scale process considerable variations of reagent dosage and pH values were observed. The effects of dissolved SO_2 (present in smelter effluents) on metal sulfide precipitation were also established.

Process Chemistry

The extent of metal sulfide precipitation is expected to be a function of pH, type of metal, sulfide dosage, and other interfering ions (such as dissolved SO_2, SO_3^{2-}) that might be present. The following types of reactions take place in the sulfide reaction tanks:

$$M^{2+} + S^{2-} \rightleftharpoons M\,S\ (Solid)$$

M = Hg, Cu, Cd, Pb, Zn

With arsenic (III) the primary reactions are:

$$As_2O_3 + 3\,S^{2-} + 3H_2O \rightleftharpoons As_2S_3\ (Solid) + 6\,OH^-$$

If the pH is allowed to rise above 6, As_2S_3 solubilizes as:

$$2\,As_2S_3\ (Solid) + 2H_2O \rightleftharpoons 3H^+ + As_3S_8^{3-} + HAsO_2$$

HgS, As_2S_3, CuS, CdS, and PbS can be completely precipitated even at pH 2, whereas ZnS precipitation would be incomplete at pH < 5. Figure 2 shows

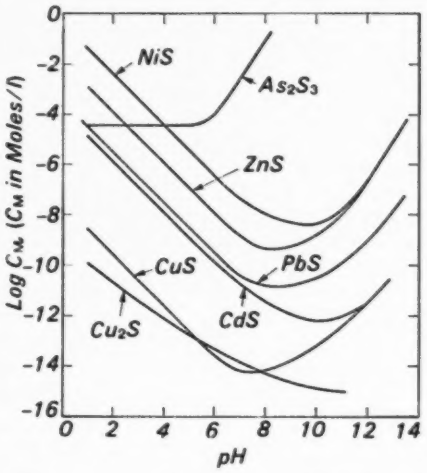

Figure 2. *Calculated solubilities of metal sulfides as a function of pH.*

the theoretical solubilities (calculated with a computer program which included all possible reactions) of various metal sulfides. Except arsenic, the solubilities of other metals decrease with an increase in pH values. Arsenic precipitates only in acidic pH. In the presence of dissolved sulfur dioxide, side reactions between *sulfite* (SO_2, SO_3) and sulfide will also consume some Na_2S reagent to form elemental sulfur and thiosulfate ($H_2SO_3 + 2H_2S \rightarrow 3S + 3H_2$); $4HSO_3^- + 2HS^- \rightarrow 3S_2O_3^{2-} + 3H_2O$). These reactions are particularly important for metals with higher solubility (such as, ZnS) in the acidic pH values.

Results and Discussions

For the five full-scale test runs the combined (process water + wash water) inlet concentrations (in mg/l) of metals were: As = 130-450, Cu = 3-5, Pb = 20-40, Cd = 3-16, Zn = 30-60, Hg = 2-4, Fe = 5-20, Sulfite = 600-1000, Sulfate = 1500-2000, and Fluoride = 90-130. The five tests represented typical operation on five separate days, with no deliberate attempt to vary operating conditions. Table 1 summarizes the operating conditions for the five tests. The sulfide precipitation pH was in the range of 3.7 to 4.8 and the CaF_2 precipitation pH was in the range of 11.2 to 11.5. The approximate sodium sulfide addition rate (in mg/l of wastewater) ranged between 400 to 900 mg/l. This corresponds to Na_2S dosage fluctuations of 0.8 to 3 times the theoretical stoichiometric dosages.

Figures 3 and 4 show the results of the two long-test runs at various sampling points. Point 7 corresponds to the sulfide precipitation effluent, whereas Point 8 corresponds to the effluent from the entire treatment process. The multilayer filter effluent contained less than 2 mg/l suspended solids, hence the soluble and total concentrations at Point 7 were approximately the same. The thickener solid removal efficiency was about 92%. Figures 3 and 4 show that during sulfide precipitation no significant improvement in soluble metal concentrations is observed after reaction tank II. Hg, Cu, Cd, and Pb removal by sulfide precipitation was always excellent, whereas As an Zn separation was complete only after lime precipitation. The range of separations and treated effluent concentrations (for all five tests) from the overall sulfide-lime treatment process is shown in Table 2.

The removal of all heavy metals (except As and Zn) was excellent (> 99%) even only with Na_2S precipitation at low pH. Table 3 shows the As and Zn

Table 1. *Operating Data Summary of Heavy Metal Removal Tests*

	Test 1 ST-01	*Test 2 ST-02*	*Test 3 LT-01*	*Test 4 ST-03*	*Test 5 LT-02*
Total Inlet Rate (m^3/hr)	114	128	108	143	131
Process Water Flow Rate (m^3/hr)	40	60	31	43	39
Runoff Water Flow Rate (m^3/hr)	74	68	77	100	92
Runoff Water pH	2.4	2.7	2.3	2.3	2.9
Reaction Tank I pH	3.7	3.7	3.9	4.9	4.2
Reaction Tank II pH	3.4	4.2	4.3	4.8	4.3
Reaction Tank III pH	3.7	4.1	4.0	3.9	4.1
Thickener Overflow pH	4.0	4.0	4.0	3.8	3.8
Lime Treatment pH	11.3	11.3	11.2	11.5	11.4

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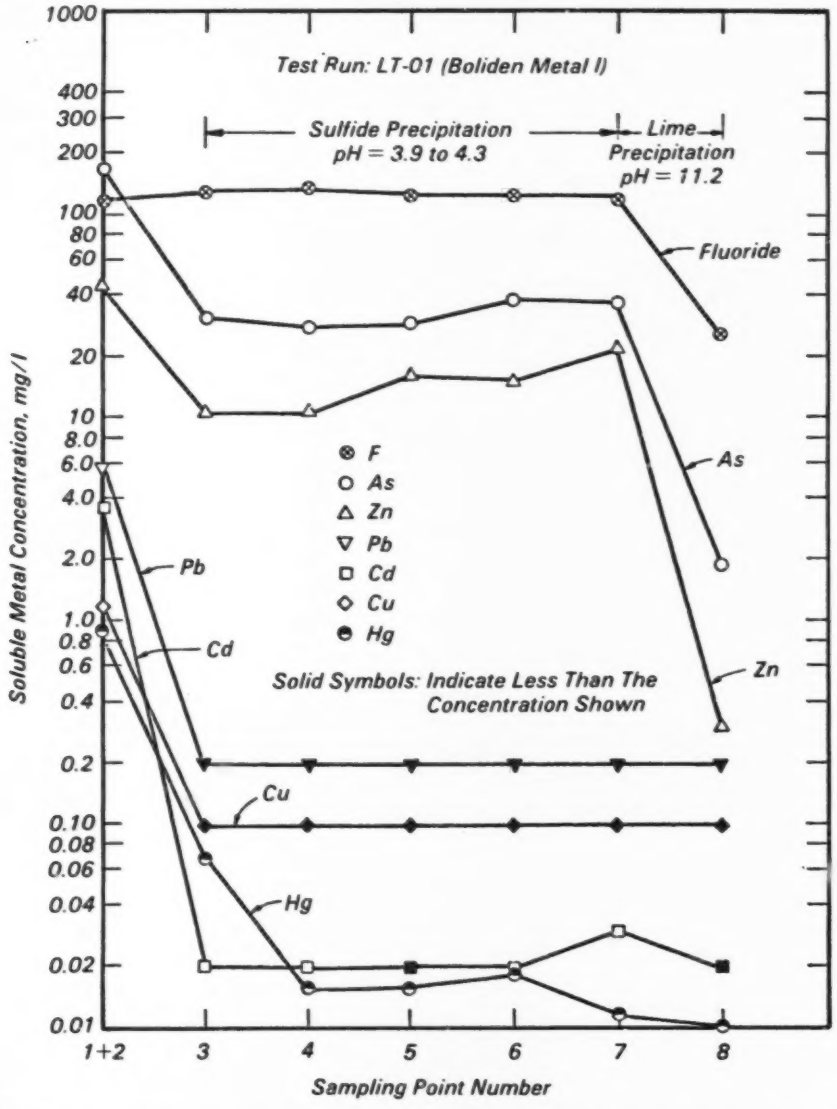

Figure 3. *Residual metal and fluoride concentrations at various sampling points (full-scale process) for test run LT-01.*

separations by the sulfide process (prior to lime precipitation step) were considerably lower. The poorer separations were due to the pH and sulfide dosage variations, and consumption of a portion of the sulfide reagent by SO_3^{2-} present in the inlet wastewater. The zero separation of zinc and poor separation of As for the ST-01 run was primarily due to the insufficient addition of Na_2S reagent.

Several observations indicated the partial disappearance of sulfide from solution through a pathway other than heavy metal precipitation. These observations were based on the facts that: (a) no H_2S gas loss from the solutions occurred, in spite of apparent stoichiometric overdoses at acidic pH values; (b) nonclosure of sulfide material balance without the consideration of thiosulfate and elemental sulfur formation; and (c) the reduction of sulfite concentration in the sulfide reaction tanks. The inlet wastewater to the sulfide precipitation plant contained high concentration (600-1000 mg/l) of sulfite. Bhattacharyya and Sun[7] have conducted extensive bench-scale studies with synthetic and Boliden Plant wastewaters to establish the effects of sulfite-sulfide side reaction, and pH variation on arsenic, zinc, and other heavy metals precipitation.

Bench-scale studies conducted at the University of Kentucky showed that proper control of pH and sulfide reagent addition are necessary for effective precipitation of arsenic and zinc. With arsenic precipitation the pH effect is more complicated because the reaction of arsenic and sulfide produces OH^- ions (by the reaction $2HAsO_2 + 3S^{2-} \rightleftharpoons As_2S_3(S) + 6OH^-$), thus instantaneous pH rise will occur unless maintained constant by acid addition. Studies with 1000 mg/l As (III) at 1.0 x Na_2S dosage showed that at pH 3 (if not maintained constant) if pH was allowed to rise before adjusting to pH 3, the residual arsenic concentration was 15 times higher (30 mg/l instead of residual As of 2 mg/l with constant pH). Figure 5 (conducted with actual Boliden wastewater) shows that arsenic precipitation is best at low pH, whereas Zn precipitation is best above pH 5. Hence a two-stage precipitation (with As_2S_3 removal in the first stage) would be most ideal.

The removal of heavy metals in the presence of high sulfite is required in various industrial wastewaters. Extensive bench-scale studies conducted with As, Zn, and other heavy metals in the presence of 0-1000 mg/l SO_3 showed that at pH < 5, side reaction between sulfite and sulfide consumed a significant portion of the Na_2S reagent particularly during precipitation of metals of higher solubility (such as ZnS, NiS). Figure 6 shows the reduction of SO_3 (by sulfide reaction) concentration and the resultant formation of thiosulfate during ZnS precipitation at pH 3. Table 4 shows (experiments with single salts) that for metals with low solubility product (such as, CuS) M^{2+} -S^{2-} reaction predominates over SO_3^{2-}-S^{2-} reaction. Higher reaction pH also reduced the importance of sulfite-sulfide reaction. Results with actual Boliden wastes showed that if the reaction was carried out at pH 4 with 1.0X stoichiometric dosage Zn residuals can be reduced to 5-7 mg/l (instead of 15-36 mg/l Zn obtained with full-scale tests). The consumption of sulfide by sulfite was also verified in two special full-scale tests, which showed the formation of thiosulfate and elemental sulfur in the reaction

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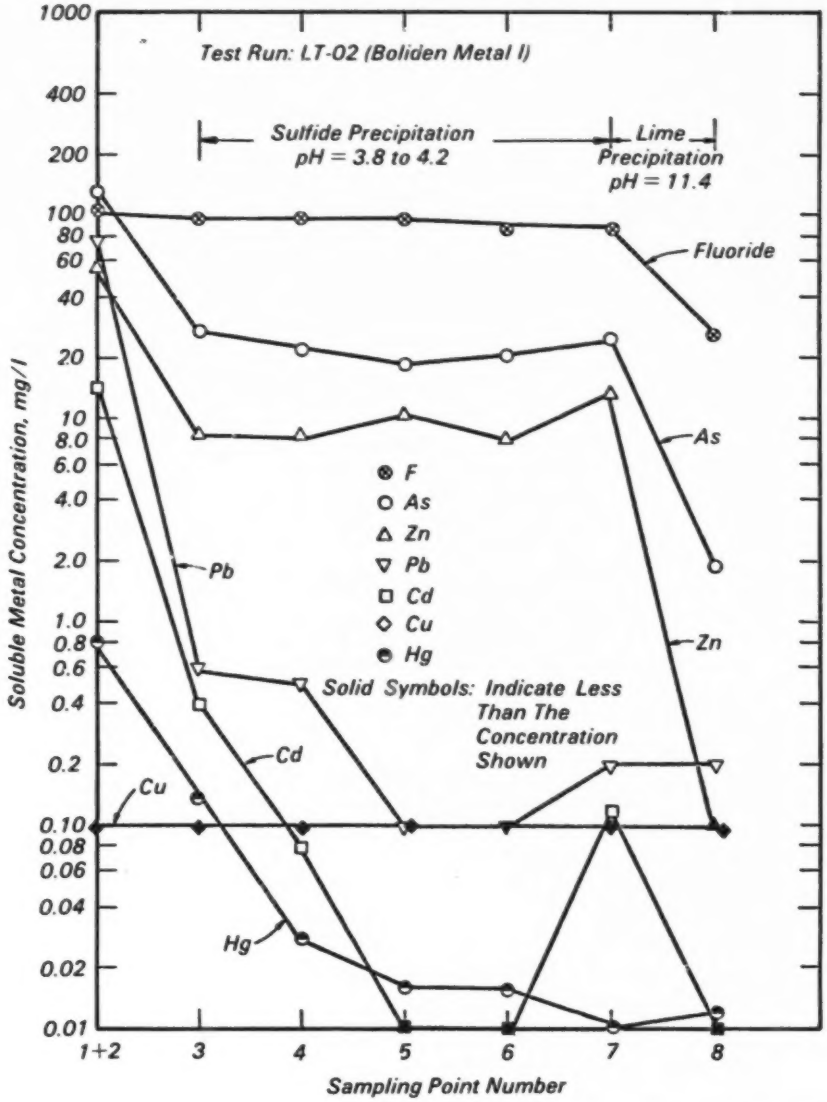

Figure 4. *Residual metal and fluoride concentrations at various sampling points (full-scale process) for test run LT-02.*

Table 2. *Overall Removal of Metals by Sulfide-Lime Precipitation Process (Full-Scale Process)*

Component	*% Removal*	*Effluent Concentration, mg/l*
As	*96 to 99*	*1.8 to 4.1*
Cu	*> 90*	*< 0.1*
Pb	*97 to 99*	*0.1 to 02.*
Cd	*99*	*0.01*
Zn	*99*	*0.1 to 0.3*
Hg	*99*	*0.008 - 0.01*
F	*70 - 78*	*20 to 34*

products. Laboratory results also showed that with excess Na_2S dosages (>1.4X) the sulfide not consumed by metal precipitation reacted with sulfite to form primarily elemental sulfur.

Summary and Conclusions

The full-scale data provided the following results: (a) the combined sulfide-lime precipitation process provided excellent removals for all heavy metals and arsenic; (b) with sulfide precipitation (no lime treatment) process at pH 3.5-5.0 although Cu, Cd, Hg, and Pb removals were excellent (98-99%), arsenic and zinc removals were not always satisfactory due to improper operating conditions and sulfite-sulfide reactions; (c) excess sulfide dosage caused no H_2S odor problem because of the presence of dissolved SO_2 in wastewater (excess sulfide reacts with sulfite to form thiosulfate and sulfur); (d) anionic polymer provided excellent flocculation of sulfide precipitates; and (e) sulfide sludge was easy to dewater; vacuum filtration provided 25-30% solids. Laboratory studies (bench-scale) showed that proper control of pH (particularly for As precipitation) and sulfide reagent addition improved arsenic and zinc precipitation. The side reaction between sulfite-sulfide consumed a significant portion of the Na_2S reagent (to form thiosulfate and sulfur) particularly during precipitation of metals of higher solubility (such as ZnS).

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Table 3. *Arsenic and Zinc Removals by Sulfide Process (Full-Scale Process)*

Test Number	Na_2S Dosage	Reaction pH	% Removal As	% Removal Zn
LT-01	≈2.7X*	3.9-4.3	78	51
LT-02	≈3.1X*	4.1-4.3	82	75
ST-01	≈0.8X*	3.4-3.7	67	0
ST-02	≈2.0X*	3.7-4.2	87	69
ST-03	≈0.9X*	3.9-4.9	78	55

*Even with excess Na_2S no H_2S gas was formed because of sulfite-sulfide reactions.

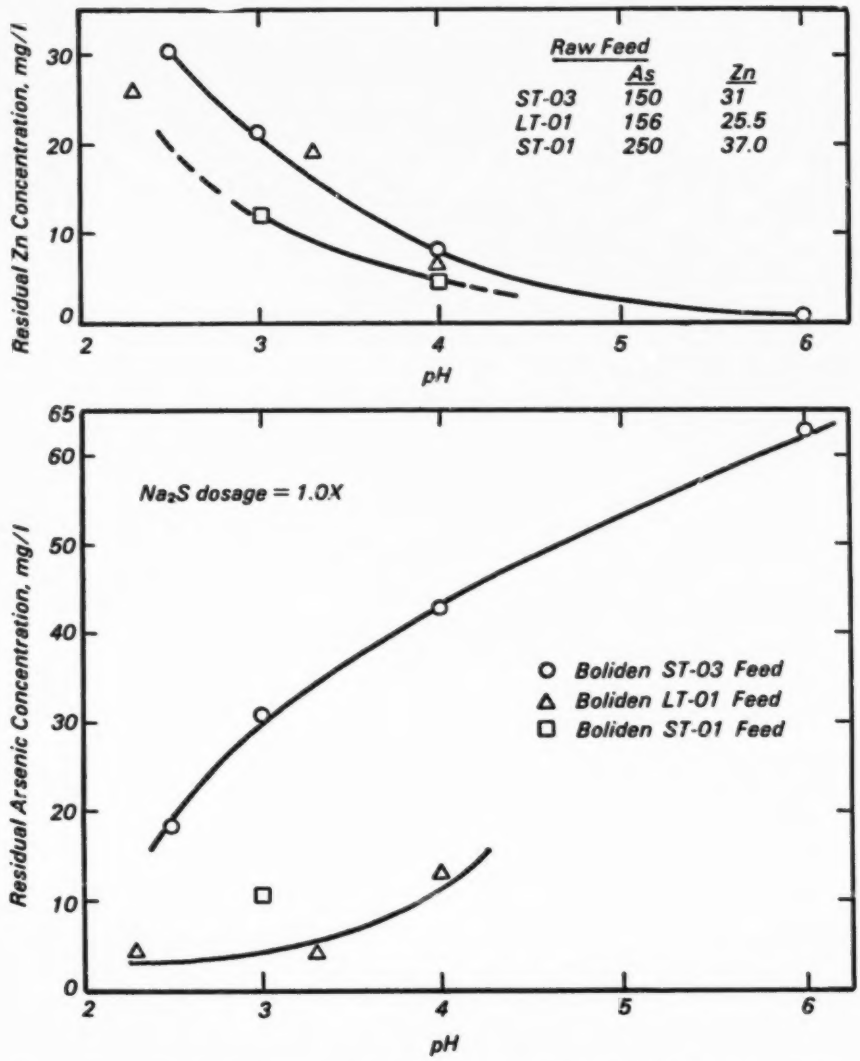

Figure 5. *Residual arsenic and zinc concentrations after sulfide precipitation (bench-scale process).*

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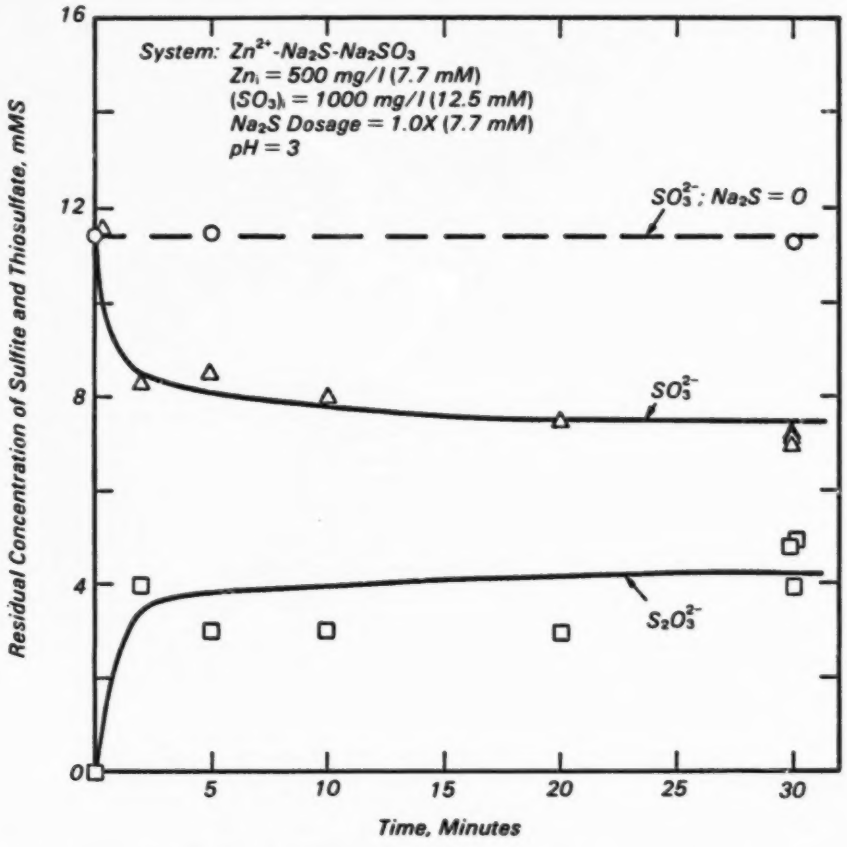

Figure 6. *Consumption of sulfite by sulfide during ZnS precipitation in the presence of Na_2SO_3 (bench-scale process).*

Table 4. *Consumption of Sulfide by Sulfite During Metal-Sulfide Precipitation*

Initial metal concentration = 100 mg/l
Initial Na_2SO_3 concentration = 1000 mg/l
Na_2S dosage = 1.0X

System	Reaction pH	% Sulfide Consumed by Sulfite
Zn^{2+}-Na_2S-Na_2SO_3	3	33.6
	4	12.8
As(III)-Na_2S-Na_2SO_3	3	2.1
Cu^{2+}-Na_2S-Na_2SO_3	3	<0.1

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The complete report, entitled "Characterization of Boliden's Sulfide-Lime Precipitation Plant," (Order No. PB 81-209 272; Cost: $10.50 (subject to change) will be available only from:

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